

Mobility and Persistence of Carbendazim and Thiabendazole Applied to Soil via Drip Irrigation

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Contribution 175-E, 1978 series, from the Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel.

Accepted for publication 5 June 1979.

ABSTRACT

SOLEL, Z., D. SANDLER, and A. DINOOR. 1979. Mobility and persistence of carbendazim and thiabendazole applied to soil via drip irrigation. *Phytopathology* 69:1273-1277.

The initial distribution, and subsequent mobility, and persistence of benzimidazole fungicides applied via a drip irrigation system to soil in a lemon grove were studied. Carbendazim applied either in solution or suspension was restricted to the 0- to 10-cm layer around the dripper. Sixty to 80% of the fungicide in soil was degraded within 4 wk. Initially, thiabendazole (TBZ) was more uniformly distributed in the soil and subsequently was moved more by leaching than was carbendazim. The TBZ persisted in soil for 22 wk, carbendazim for 10 wk. The uptake of either fungicide by lemon trees under field conditions was minute and did not affect the severity of mal secco disease. In laboratory tests, the leaching of

solutions or suspensions of carbendazim in soil columns was insignificant either in dry or wet soil: 85-95% of the applied dose remained in the 0- to 5-cm layer after leaching with water equivalent to 630 mm of rain. In laboratory degradation tests in two soil types, either autoclaved or not carbendazim lasted 9 mo and had a half-life of 4-6 mo. Water extraction of soil amended with carbendazim yielded approximately 3 µg/ml. When applied as a drench to soil in pots, carbendazim was taken up by Rough lemon seedlings and accumulated in leaves in amounts up to 40 µg/g leaf tissue. Degradation of the toxicant in leaves was 10% in 35 days. The leaves were completely protected against *Phoma tracheiphila*.

Additional key words: pesticides in soil.

Carbendazim (methyl 1*H*-benzimidazol-2-ylcarbamate) and thiabendazole (2-[4-thiazolyl] benzimidazole) both are derivatives of benzimidazole and are inhibitory to *Phoma tracheiphila* (Peri Kantschaveli & Gikachvili (19), which causes mal secco, a vascular disease of citrus. When benzimidazole fungicides are sprayed on citrus foliage, only a limited amount is taken up by the plant and exhibits systemic fungicidal activity (20,21), but when applied to citrus roots, these fungicides are effectively taken up and readily translocated to the foliage. Uptake by roots has been demonstrated in hydroponic culture (13,22) and with plants grown in soil in pots (11,17,19). However, under natural field conditions benzimidazole fungicides drenched into the soil are barely detectable in many plants, and least of all in trees. The inefficiency of drench application of benzimidazole fungicides might be related to their limited mobility in the soil (2,5,8,10,15). They are adsorbed to soil (1,3), but the relative importance of this in limiting mobility has not been elucidated. Various values describing the persistence of benzimidazole fungicides in soil (mainly under laboratory conditions) have been reported (2-5), but their relevance to field performance has not been established.

We have attempted to overcome some of the barriers encountered with soil drench application of benzimidazole fungicides by using a drip irrigation system to apply and leach the fungicides in a lemon grove. Drip irrigation wets the soil only around the dripper and mainly to a depth of 30 cm. Furthermore, an extremely dense root system rich in rootlets is developed in the wetted area which enables efficient uptake. A single massive treatment aimed at oversaturating soil adsorption and forming a reservoir for prolonged root uptake was compared with a continuous application. The experiment was conducted in a lemon grove infected with *P. tracheiphila* in the hope that the results would be applicable for the control of the disease. The distribution of the fungicides within the trees, and the infection severity, were monitored. Complementary studies were conducted in the greenhouse to assess the concentration of carbendazim required within leaf tissue to confer protection against *P. tracheiphila*, and to evaluate the persistence of the toxicant in lemon foliage.

Measures to enhance carbendazim mobility in soil were evaluated in laboratory tests. Carbendazim was selected for these studies because it has higher in vitro toxicity than thiabendazole (19).

MATERIALS AND METHODS

Fungicides. Carbendazim was used in two formulations, wettable powder (Bavistin, 50% a.i., BASF AG, Ludwigshafen, Germany) and solution in 1.0 N hydrochloric acid (1.5% a.i.). Thiabendazole (TBZ) was applied as flowable concentrate (Tectoril 40, 40% a.i., Merck & Co., Inc. Rahway, NJ 07065).

Soils. The soils used in the study were Ha'Kfar Ha'Yarok sandy loam (low in organic matter) of the experimental lemon grove; and Bet Dagan sandy clay loam (rich in organic matter) of the Central Farm (Table 1).

Extraction and quantitative assays of fungicides. Soil samples (10-50 g) were extracted with methanol (50-100 ml) by stirring overnight and bioassaying the filtrate. The fungicide content was calculated on the basis of the soil dry weight. Recovery of known amounts of fungicides in soil ranged 70-90%. Leaves (5 g) were extracted by homogenizing the methanol (50 ml) with an Ultraturax (Janke & Kunkel KG, Staufen, Germany); then the filtrate was concentrated by flash evaporation and bioassayed. The bioassay procedure was based on comparison of inhibition zones with those caused by known standards of carbendazim and TBZ in cultures of *Penicillium* sp. and *Verticillium dahliae*, respectively (18). To quantify fungicide content in the wood, a modified bioassay technique was used (14). The carbendazim metabolite, 2-aminobenzimidazole (2-AB), was analyzed chemically (6).

Application of fungicides via drip irrigation. The experiment was carried out in a 15-yr-old lemon grove (cultivar Eureka) at Ha'Kfar Ha'Yarok. The irrigation system consisted of two plastic pipes laid along the rows, each passing 0.5 m from the trunks. The drippers (Netafim, Hazerim, Israel), each with a capacity of 4 L/hr, were spaced 1 m apart; every tree was irrigated by eight drippers. The wetting profile per dripper is illustrated in Fig. 1. For the application of fungicides, a fertilization tank connected to the irrigation system was used. Massive doses (128 g per tree) of carbendazim formulations and TBZ were applied

to six trees each in a single dose (16 g per dripper). A similar dose of carbendazim solution also was applied in 12 weekly treatments of 10.66 g per tree. The plot was irrigated weekly throughout the summer, with 500 L per tree. At timed intervals the soil of two drippers was sampled with an auger (2.5 cm diameter) at various distances and depths from the dripper (Fig. 1). Two leaf samples of 15 g per tree were collected during the experiment. Seventeen weeks after treatment, holes 8 mm in diameter and 6 cm deep were drilled in the trunk and the sawdust was collected for fungicide assay.

Leaching of carbendazim in soil columns. Bet Dagan soil (Table 1) was air-dried, sieved, and packed in a 50 × 5 cm plastic column, resulting in a soil column height of 40 cm. Carbendazim solution or suspension (20 mg in 10 ml) was drenched onto air-dry or wet (field capacity) soil. Soon after treatment, and thereafter at 5-day intervals, the soil was leached with 150 ml water (equivalent to 90 mm of rain). After four and seven applications of water, the soil was extruded from the columns (two replicates of each treatment), segregated into five sections, and its fungicide content was determined.

TABLE 1. Properties of the soils used in the study of fungicide mobility and persistence

Soil name	Texture	Soil Fraction (% of total)					pH
		Coarse sand	Sand	Silt	Clay	Organic matter	
Ha'Kfar							
Ha'Yarok	Sandy loam	25.0	54.6	6.8	13.6	1.4	8.1
Bet Dagan	Sandy clay loam	12.1	48.6	14.0	25.3	4.5	8.0

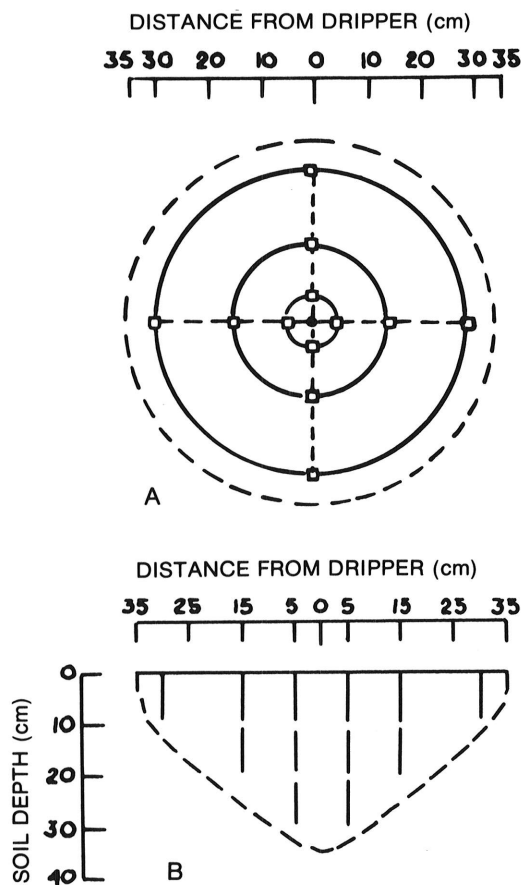


Fig. 1. The wetting profile produced by a drip irrigation dripper and the positions of soil sampling in A, horizontal and B, vertical views. Broken line indicates the wetting zone; squares and vertical lines illustrate position and layer depth of soil sampling.

Persistence of carbendazim in soil. Bet Dagan and Ha'Kfar Ha'Yarok soils (500 g) autoclaved for 1 hr or not autoclaved, in 500-ml beakers, were amended with approximately 500 mg of carbendazim (four replicates) by thorough mixing. The soils were wetted with sterile water and moisture was added from time to time during the experiment. The beakers were covered with aluminum foil without sealing and maintained in the laboratory for 260 days. At timed intervals each beaker was sampled (10 g) and the soil was bioassayed for carbendazim.

Release of carbendazim from soils into water. This test was combined with the study mentioned above on persistence of carbendazim. Samples (10 g, four replicates) were taken at timed intervals from the soils that were not autoclaved, suspended in 100 ml of water and stirred overnight at room temperature. The water extract was filtered and bioassayed for carbendazim.

Uptake from soil and persistence of carbendazim in lemon seedlings. Sixteen pots (5 kg sandy loam, 22 cm diameter) of 2-yr-old seedlings of Rough lemon grown in a greenhouse were drenched with 1,000 mg of carbendazim (in 1,000 ml of water). At timed intervals over 73 days, leaves were sampled for content of carbendazim and its metabolite, 2-aminobenzimidazole (2-AB). After 73 days, the seedlings were removed from the soil, their roots were washed thoroughly with water and placed in Hoagland's solution. At timed intervals of up to 35 days, two seedlings were removed and analyzed for carbendazim or 2-AB in leaves, stem, and roots.

Control of mal secco in potted lemon seedlings by carbendazim drench. One-year-old seedlings of Rough lemon grown in pots (1 kg sandy loam, 10 cm in diameter) were drenched with 119 mg carbendazim (in 125 ml of water). Five days later leaves of treated and untreated plants (four of each) were inoculated (at four points on four leaves) with *Phoma tracheiphila* (19). Thirty and 70 days after treatment the infection status and fungicide content in the leaves were examined.

RESULTS

Field trials. The weekly applications of carbendazim resulted in greatly restricted distribution and in scant accumulation of the fungicide in the vicinity of the dripper (Fig. 2). Concentration in the soil was low (less than 10 µg/g) and the fungicide disappeared completely soon after the termination of treatments. The massive single-dose treatment with carbendazim resulted in very limited initial distribution in the soil both horizontally and vertically, regardless of the liquid or powder formulation of the toxicant (Fig. 3, 4). A week after application the concentration of the fungicide was more than 500 µg/g soil in the upper 10-cm layer near the dripper and less than 20 µg/g soil at a horizontal distance or depth of 10 cm

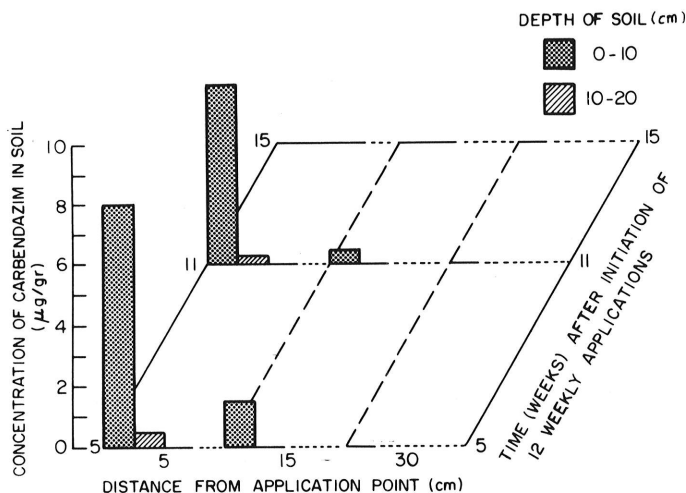


Fig. 2. Distribution and persistence of carbendazim in soil at various time intervals after the initiation of 12 weekly applications (each of 1.33 g carbendazim solution [total, 16 g] per dripper) via drip irrigation.

from the dripper. Mobility of the fungicide was not enhanced by weekly drip irrigation following the treatment. The persistence of carbendazim in the soil was short; 60–80% of the content was lost between the 1st and the 4th wk, and degradation was nearly complete within 10 wk after application (Fig. 3,4).

TBZ in a single dose showed appreciable vertical and horizontal distribution in the soil (Fig. 5), though mostly limited to the vicinity of the dripper. Beneath the application point, a considerable concentration was found in the 20- to 30-cm layer (31 $\mu\text{g/g}$ soil). In time, the fungicide had moved laterally 30 cm from the application point (19 $\mu\text{g/g}$ soil after 15 wk), and it was detected in the 30- to 35-cm layer beneath the dripper. Degradation of TBZ was relatively moderate as some of it, 16 $\mu\text{g/g}$ soil in the upper 10-cm layer near the dripper, persisted at the end of the experiment, 22 wk after application.

Uptake of both fungicides by the lemon trees was minute. Assays of leaves sampled every few weeks revealed none of either fungicide, except for occasional traces (0.2 $\mu\text{g/g}$ fresh weight). The presence of the fungicides in the wood of the trunks was assayed at the end of the experiment. The TBZ content was approximately 10 $\mu\text{g/g}$ fresh weight, while carbendazim was not detected under any treatment. The severity of mal secco increased during the season, and at autumn there was no difference between the treated and the control trees.

Laboratory experiments. After leaching soil columns with four or seven aliquots of water, 150 ml each (equivalent to 90 mm of rain), the movement of carbendazim, applied as a wettable powder or in solution to dry or wet soil, was very limited; 85–95% of the applied dose remained in the upper 5-cm layer (Fig 6). The amount of fungicide in the soil diminished sharply with soil depth. There was no appreciable difference in the movement of carbendazim in either of the two formulations applied to dry or wet soil.

Degradation of carbendazim in Bet Dagan and Ha'Kfar Ha'Yarok soils either autoclaved or not was slow and gradual (Fig. 7), without any distinct effect of soil type or heat treatment. The half-life of carbendazim was about 4–6 mo.

Availability of carbendazim in soil for root uptake was inferred from the amount found in the water extract of treated soil. The concentration of carbendazim in the water extract (Table 2) in both soil types was steady for 40 days (approximately 3 $\mu\text{g/ml}$) and dropped thereafter (1.8 $\mu\text{g/ml}$). The amounts of fungicide in the water extract (18–44 $\mu\text{g/g}$ soil), which may be available for root uptake, are less than 10% of the dose mixed with the soil (510–525 $\mu\text{g/g}$ soil).

Carbendazim, added as drench to soil (200 $\mu\text{g/g}$ soil) in pots in which Rough lemon seedlings were grown, was taken up by the plants and gradually accumulated in the leaves, up to a maximum of 40 $\mu\text{g/g}$ leaf tissue at 73 days after treatment (Fig. 8). At that time only traces of the fungicide were found in the roots and none was detected in the stem. The major breakdown product, 2-AB, was found in the leaves only in low amounts (Fig. 8). When the plants were transferred to a nutrient solution without carbendazim, slow degradation of the fungicide was noted.

In a similar experiment, soil was drenched with carbendazim solution (119 $\mu\text{g/g}$ soil) and leaves of the lemon seedlings were inoculated 5 days later with *Phoma tracheiphila*. None of the treated plants became infected but all the untreated control plants were infected. The content of carbendazim in leaves 30 and 70 days after treatment was 32 and 50 $\mu\text{g/g}$ of leaf tissue, respectively.

DISCUSSION

The inefficient field control of tree diseases by benzimidazole fungicides applied in soil drenches has been challenged in this work by using drip irrigation. However, treatment with either benzimidazole fungicide did not control mal secco of lemon. In the trunk, only TBZ was accumulated to any extent, 10 $\mu\text{g/g}$ wood and that concentration was shown in a bioassay evaluation (19) to be only moderately inhibitory to *P. tracheiphila*. Carbendazim and TBZ were barely detectable in the leaves of trees in the field (0.2 $\mu\text{g/g}$ tissue), while in the potted seedlings where infection was

TABLE 2. Concentration of carbendazim in water extract (10:1) of amended soil after various incubation periods

Time interval (days)	Concentration of carbendazim ($\mu\text{g/ml}$)	
	Sandy loam ^a	Sandy clay loam ^b
0	2.7	2.9
1	3.3	3.3
10	3.3	3.6
20	4.4	3.9
40	2.9	3.2
80	1.8	1.8

^aSoil was amended with 510 μg carbendazim per gram of soil.

^bSoil was amended with 525 μg carbendazim per gram of soil.

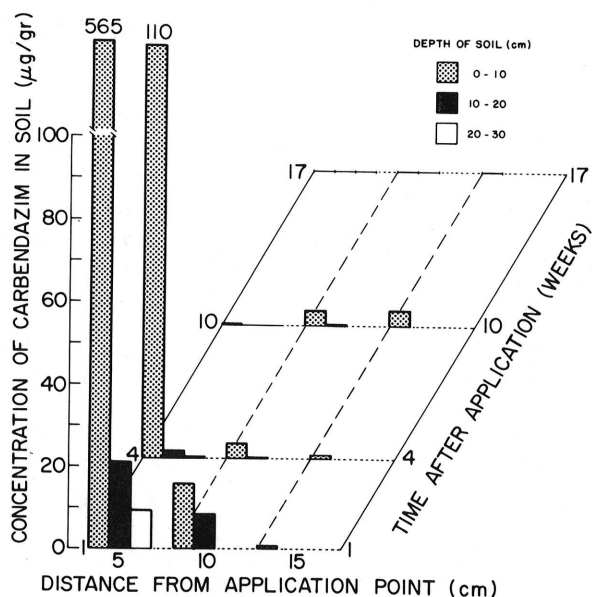


Fig. 3. Distribution and persistence of carbendazim in the soil at various time intervals after a single application of carbendazim solution via drip irrigation, 16 g per dripper.

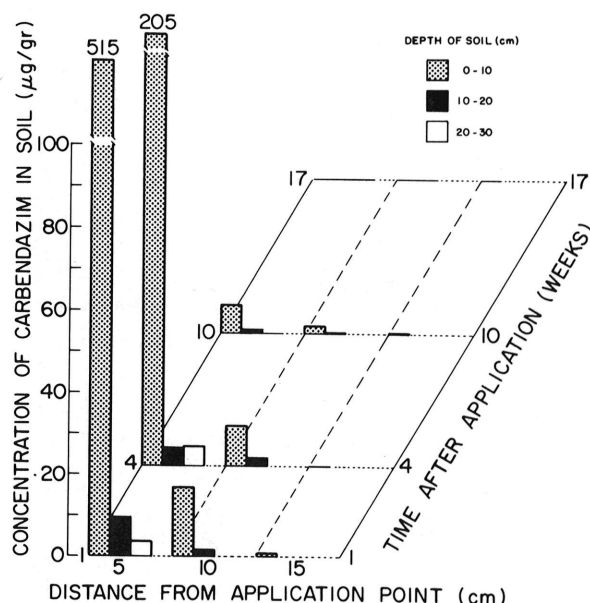


Fig. 4. Distribution and persistence of carbendazim in the soil at various time intervals after a single application of carbendazim suspension via drip irrigation, 16 g per dripper.

completely prevented we found concentrations of carbendazim ranging 32–50 $\mu\text{g/g}$ of leaf tissue. Degradation of carbendazim within the lemon plant was shown to be slow.

The greenhouse experiments with treated seedlings and the carbendazim content in water extracts from amended soil indicated that if carbendazim had reached the rhizospheres of the trees in the grove it would have been taken up. Two factors, the much restricted movement of the fungicides in the soil under field conditions and also in soil columns, and their rapid degradation in the field may

account for the failure of the treatment in the lemon grove. Mobility of pesticides in soil is influenced by their solubility and by adsorption to soil constituents (8). Adsorption of both carbendazim and TBZ has been demonstrated (3). However, a portion of the chemical might be desorbed and subjected to

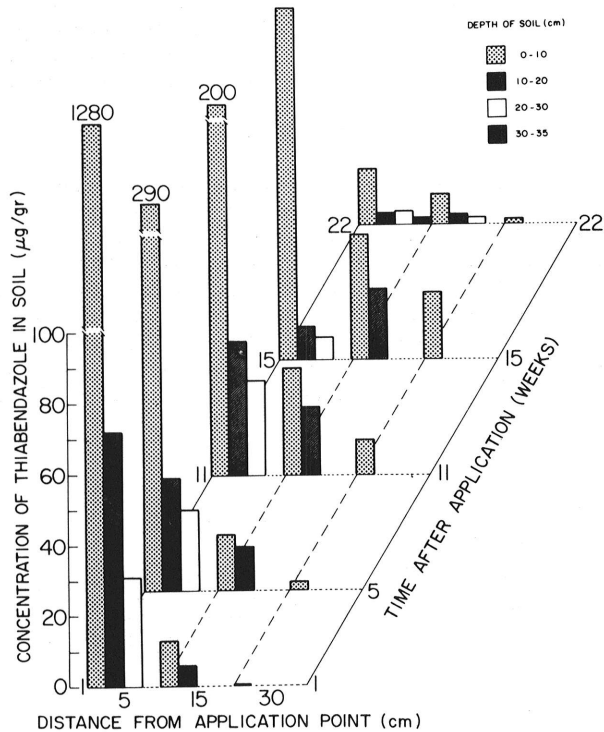


Fig. 5. Distribution and persistence of thiabendazole in soil at various time intervals after a single application of thiabendazole suspension via drip irrigation, 16 g per dripper.

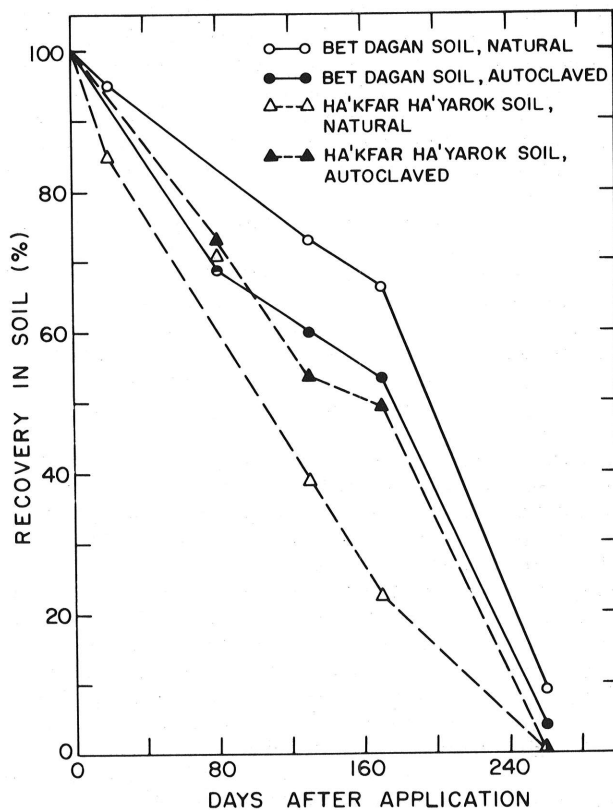


Fig. 7. Persistence of carbendazim in two types of soil, either autoclaved or nonautoclaved (natural), supplemented with 500–525 μg carbendazim per gram of soil.

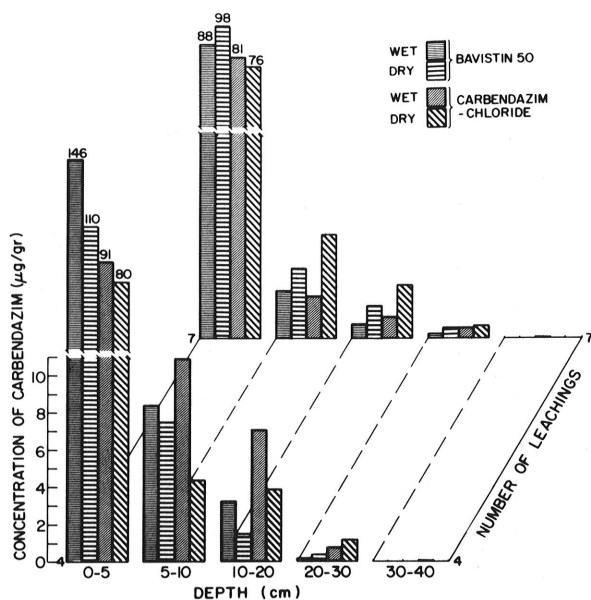


Fig. 6. Leaching of carbendazim in sandy clay loam after application as water suspension or solution to dry or wet (at field capacity) soil. The soil in columns was leached with aliquots of water, each equivalent to 90 mm of rain.

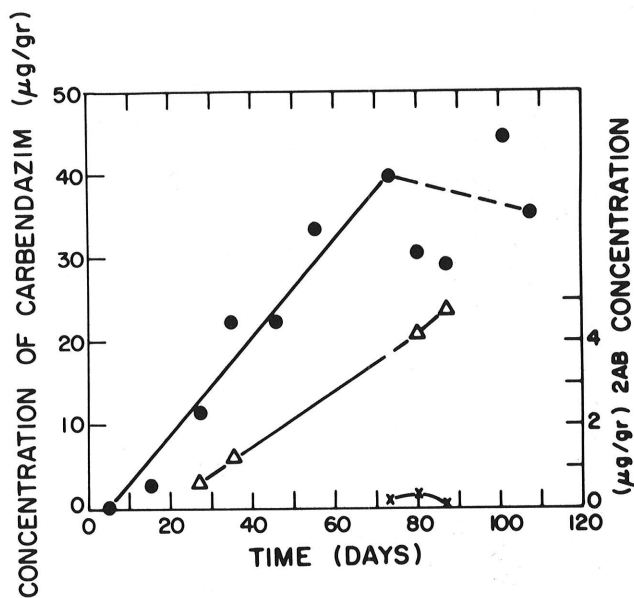


Fig. 8. Accumulation and disappearance of carbendazim and its metabolite 2-aminobenzimidazole (2-AB) in lemon seedlings grown in pots after drench application of carbendazim (200 $\mu\text{g/g}$ soil). Seventy-three days after treatment, the seedlings were transferred from the pots to untreated nutrient solution. Legend: ●—● carbendazim in leaves, ×—× carbendazim in roots, and △—△ 2-AB in leaves.

leaching. When carbendazim treatment was subdivided into 12 weekly applications, some soil penetration occurred. However, the rate of movement in that treatment was clearly inferior to that in the single large-dose treatment that had oversaturated the available sorption sites in the upper soil profile, which enabled leaching of the unrestricted excess chemical. Such leaching, at a concentration equal to the water solubility, is expected until the lower soil also becomes saturated. Since both carbendazim and TBZ have low water solubility (less than 10 and 50 $\mu\text{g}/\text{ml}$, respectively) this effect of overloading would be limited, but TBZ could be more mobile. In the field test TBZ showed better mobility; it penetrated to a depth of 35 cm, and also showed some lateral dispersion. For some pesticide groups, mobility in soil was shown to be correlated with solubility (7).

The superior mobility of TBZ also could be due to longer persistence than carbendazim under field conditions, 22 vs 4 wk. The superior persistence of TBZ already has been demonstrated in the field (10) and in laboratory studies (3). The half-life period of carbendazim in the experimental plot, less than 4 wk, is much shorter than the 3-6 mo (5) or 11 wk (4) reported on a planted soil. The more rapid catabolism of carbendazim in the experimental plot can be attributed to high summer temperatures (above 30 C every day [10]) and the alkalinity of the soil, which was found by Austin and Briggs (4) to be a dominant factor in the degradation of this fungicide. Soil microflora has been suggested to be the major factor in benomyl decomposition (9,16). In our studies the rate of decomposition of carbendazim was the same in autoclaved and nonautoclaved soil, apparently due to the extremely high doses used in our tests. Thus, it appears that in agreement with our field studies, chemical decomposition was the dominant process. The rates of carbendazim disappearance in the field, without a considerable uptake by the trees, do not conform with our laboratory tests, in which persistence was much longer. Factors such as higher temperature, sun irradiation, or certain moisture conditions in soil in the orchard may play a crucial role in carbendazim degradation.

Controversial results were reported for penetration of pesticides in irrigation water into soil previously wetted or left dry (8,12). Our results with carbendazim did not reveal any effect of pretreatment soil moisture.

Munnecke (12) evaluated the movement of 13 fungicides in soil columns and concluded that penetration of solution formulations was greater than that of suspensions. Pitblado and Edgington (15) doubled the depth of soil penetration by benomyl in water suspension by solubilizing it with acidic adjuvants. Our results, both with soil in columns and under field conditions, revealed no meaningful difference in mobility of either carbendazim formulation, because under the basic reaction of our soils the solution is neutralized and the toxicant salts out.

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